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## Note

### Glass capillary gas chromatography of homologous series of esters

#### Separation of homologous series of esters of halogenated carboxylic acids on a glass capillary column with the non-polar stationary silicone phase OV-101

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Few papers have been published on the capillary gas chromatography of homologous series of halogenated esters of carboxylic acids. Jamieson and Reid<sup>1</sup> separated trifluoroacetates of aliphatic alcohols on capillary columns coated with EGSS-X, BDS and DEGS. Recently, systematic capillary gas chromatography of homologous series of halogenated esters of *n*-carboxylic acids has been reported by Korhonen<sup>2-4</sup>. Our earlier works<sup>5-11</sup> dealt with the gas chromatography of homologous series of halogenated esters containing fluorine, chlorine, bromine and iodine atoms in either the alcohol or the acid moiety of the ester on packed columns with five different polar stationary phases. This problem has now been solved using glass-capillary gas chromatography. Retention indices, *I*, and increments of retention indices,  $\Delta I_x$ , were used to correlate the type and number of halogens in the acid moiety of the ester molecule.

This paper describes a study of the gas chromatography of mixtures of homologous series of  $C_1$ - $C_{16}$  *n*-alkyl and  $C_3$ - $C_5$  isoalkyl acetates (Ac), monochloroacetates (MClAc), dichloroacetates (DCIAc), trichloroacetates (TCIAc), monobromoacetates (MBrAc), monoiodoacetates (MIAc) and trifluoroacetates (TFAc).

The column temperature was maintained at 80°C for the lower esters and at 200°C for the higher ones.

#### EXPERIMENTAL

Analyses were performed on a Fractovap Model 2150 gas chromatograph (Carlo Erba, Milan, Italy), equipped with a flame-ionization detector and a home-made glass capillary column (15 m × 0.22 mm I.D.) coated with OV-101 by a dynamic method. The glass capillary column was prepared from soft soda-lime glass (Unihost, Jablonec, Czechoslovakia). The inner walls were roughened by the method of Onuska *et al.*<sup>12</sup> and deactivated with dimethyldichlorosilane by a static method at 220°C. Nitrogen was used as carrier gas at a flow-rate of 10-30 cm/sec. The splitting ratio was 1:150. The temperatures of the injector and detector were 250 and 300°C, respectively, for separation of the higher esters. The column temperature was maintained at 80°C for the lower ( $C_1$ - $C_6$ ) and at 200°C for the higher ( $C_6$ - $C_{16}$ ) esters. The

retention times of methane, the esters and of the *n*-alkanes used for the calculation of retention indices were measured with a stopwatch.

### Samples

Mixtures of halogenated acetates were prepared from the individual esters. Halogenated esters were prepared by azeotropic esterification. Acetates were obtained by the usual sulphuric acid-catalysed esterification of commercial acetic acid. Their synthesis was described earlier<sup>6,7</sup>.

### RESULTS AND DISCUSSION

The influence of the type and number of halogens in the acid moiety of  $C_1$ – $C_{16}$  *n*-alkyl and  $C_3$ – $C_5$  isoalkyl acetates on the retention characteristics was studied. The retention indices and their increments for single halogen atoms ( $\Delta I_X$ ) and methylene groups ( $\Delta I_{CH_2}$ ) are presented in Tables I and II.

TABLE I  
RETENTION INDICES OF  $C_1$ – $C_6$  ALKYL ESTERS AND THEIR INCREMENTS AT 80 C

<i>Esters</i>	<i>I</i>	$\Delta I_{CH_2}$	$\Delta I_{X,2X,3X}$	$\Delta I_{ICl}$	$\Delta I_{HCl}$	$\Delta I_{IHCl}$
AcC <sub>1</sub>	525.9	—	—	—	—	—
AcC <sub>2</sub>	595.7	69.8	—	—	—	—
AcC <sub>3</sub>	695.8	100.1	—	—	—	—
AcC <sub>4</sub>	796.4	100.6	—	—	—	—
AcC <sub>5</sub>	896.5	100.1	—	—	—	—
AcC <sub>6</sub>	996.6	100.1	—	—	—	—
AcisoC <sub>3</sub>	646.8	—	—	—	—	—
AcisoC <sub>4</sub>	757.2	110.4	—	—	—	—
AcisoC <sub>5</sub>	859.7	102.5	—	—	—	—
MClAcC <sub>1</sub>	729.4	—	—	203.5	—	—
MClAcC <sub>2</sub>	806.4	77.0	—	210.7	—	—
MClAcC <sub>3</sub>	902.5	96.1	—	206.7	—	—
MClAcC <sub>4</sub>	1001.4	98.9	—	205.0	—	—
MClAcC <sub>5</sub>	1100.2	98.8	—	203.7	—	—
MClAcC <sub>6</sub>	1200.8	100.6	—	204.2	—	—
MClAcisoC <sub>3</sub>	850.7	—	—	203.9	—	—
MClAcisoC <sub>4</sub>	959.6	108.9	—	202.4	—	—
MClAcisoC <sub>5</sub>	1062.5	102.9	—	202.8	—	—
DClAcC <sub>1</sub>	811.5	—	285.6	203.5	82.1	—
DClAcC <sub>2</sub>	882.4	70.0	286.7	210.7	76.0	—
DClAcC <sub>3</sub>	974.5	92.1	278.7	206.7	72.0	—
DClAcC <sub>4</sub>	1069.8	95.3	273.4	205.0	68.4	—
DClAcC <sub>5</sub>	1166.9	97.1	270.4	203.7	66.7	—
DClAcC <sub>6</sub>	1267.0	100.1	270.4	204.2	66.2	—

(Continued on p. 144)

TABLE I (continued)

Esters	<i>I</i>	$\Delta I_{CH_2}$	$\Delta I_{X,2X,3X}$	$\Delta I_{ICl}$	$\Delta I_{IICl}$	$\Delta I_{IIICl}$
DCIAcisoC <sub>3</sub>	920.8	—	270.0	203.9	70.1	—
DCIAcisoC <sub>4</sub>	1028.8	108.0	271.6	202.4	69.2	—
DCIAcisoC <sub>5</sub>	1129.6	100.8	269.9	202.8	67.1	—
TClAcC <sub>1</sub>	895.5	—	369.6	203.5	82.1	84.0
TClAcC <sub>2</sub>	961.7	66.2	366.0	210.7	76.0	79.3
TClAcC <sub>3</sub>	1051.2	89.5	355.4	206.7	72.0	76.7
TClAcC <sub>4</sub>	1144.5	93.3	348.1	205.0	68.4	74.7
TClAcC <sub>5</sub>	1240.2	95.7	343.7	203.7	66.7	73.3
TClAcC <sub>6</sub>	1339.7	99.5	343.1	204.2	66.2	72.7
TClAcisoC <sub>3</sub>	995.9	—	349.1	203.9	70.1	75.1
TClAcisoC <sub>4</sub>	1103.8	107.9	346.6	202.4	69.2	75.0
TClAcisoC <sub>5</sub>	1203.3	99.5	343.6	202.8	67.1	73.7
MBrAcC <sub>1</sub>	800.2	—	274.3	—	—	—
MBrAcC <sub>2</sub>	873.4	73.2	277.7	—	—	—
MBrAcC <sub>3</sub>	969.5	96.1	273.7	—	—	—
MBrAcC <sub>4</sub>	1067.8	98.3	271.4	—	—	—
MBrAcC <sub>5</sub>	1166.7	98.9	270.2	—	—	—
MBrAcC <sub>6</sub>	1265.8	99.1	269.2	—	—	—
MBrAcisoC <sub>3</sub>	916.2	—	269.4	—	—	—
MBrAcisoC <sub>4</sub>	1025.8	109.6	268.6	—	—	—
MBrAcisoC <sub>5</sub>	1127.9	102.1	268.1	—	—	—
MIAcC <sub>1</sub>	886.0	—	360.1	—	—	—
MIAcC <sub>2</sub>	960.5	74.5	374.8	—	—	—
MIAcC <sub>3</sub>	1056.8	96.3	361.0	—	—	—
MIAcC <sub>4</sub>	1153.5	96.7	357.1	—	—	—
MIAcC <sub>5</sub>	1251.3	97.8	354.8	—	—	—
MIAcC <sub>6</sub>	1349.9	98.6	353.3	—	—	—
MIAcisoC <sub>3</sub>	999.9	—	353.1	—	—	—
MIAcisoC <sub>4</sub>	1111.6	111.7	353.4	—	—	—
MIAcisoC <sub>5</sub>	1209.9	98.3	350.2	—	—	—
TFAcC <sub>3</sub>	569.6	—	-126.2	—	—	—
TFAcC <sub>4</sub>	664.3	94.7	-132.1	—	—	—
TFAcC <sub>5</sub>	761.0	96.7	-135.5	—	—	—
TFAcC <sub>6</sub>	858.8	97.8	-137.8	—	—	—
TFAcisoC <sub>3</sub>	528.8	—	-118.0	—	—	—
TFAcisoC <sub>4</sub>	625.4	96.6	-131.8	—	—	—
TFAcisoC <sub>5</sub>	724.9	99.5	-134.8	—	—	—

The increments of the retention indices for chlorine, bromine, iodine and fluorine atoms ( $\Delta I_{3X}$ ,  $\Delta I_{2X}$ ,  $\Delta I_X$ ) were calculated as the difference between the indices for the halogenated acetate examined and those for the corresponding unhalogenated one.

The retention increments for chlorine atoms adding to the chloroacetate and dichloroacetate molecules ( $\Delta I_{ICl}$  and  $\Delta I_{IIICl}$ ) were calculated from the differences between the retention indices of the higher-chlorine-substituted ester and the lower-substituted one, e.g.  $\Delta I_{IIICl} = I(\text{TClAcC}_1) - I(\text{DCIAcC}_1)$  and  $\Delta I_{ICl} = I(\text{DCIAcC}_1)$

TABLE II  
RETENTION INDICES OF C<sub>6</sub>-C<sub>16</sub> ALKYL ESTERS AND THEIR INCREMENTS AT 200°C

<i>Esters</i>	<i>I</i>	$\Delta I_{CH_2}$	$\Delta I_{X,2X,3X}$	$\Delta I_{ICI}$	$\Delta I_{IICI}$	$\Delta I_{IIICI}$
AcC <sub>6</sub>	991.1	—	—	—	—	—
AcC <sub>7</sub>	1091.7	100.6	—	—	—	—
AcC <sub>8</sub>	1189.4	97.7	—	—	—	—
AcC <sub>9</sub>	1289.8	100.4	—	—	—	—
AcC <sub>10</sub>	1389.2	99.4	—	—	—	—
AcC <sub>12</sub>	1589.6	200.4	—	—	—	—
AcC <sub>14</sub>	1790.6	201.4	—	—	—	—
AcC <sub>16</sub>	1991.1	200.5	—	—	—	—
MCIAcC <sub>6</sub>	1207.5	—	216.4	216.4	—	—
MCIAcC <sub>7</sub>	1307.0	99.5	215.3	215.3	—	—
MCIAcC <sub>8</sub>	1406.0	99.0	216.6	216.6	—	—
MCIAcC <sub>9</sub>	1507.2	101.2	217.4	217.4	—	—
MCIAcC <sub>10</sub>	1607.2	100.0	218.0	218.0	—	—
MCIAcC <sub>12</sub>	1807.2	200.0	217.6	217.6	—	—
MCIAcC <sub>14</sub>	2008.3	201.1	217.7	217.7	—	—
MCIAcC <sub>16</sub>	2209.8	201.5	218.7	218.7	—	—
DCIAcC <sub>6</sub>	1285.5	—	294.4	216.4	78.0	—
DCIAcC <sub>7</sub>	1385.2	99.7	293.5	215.3	78.2	—
DCIAcC <sub>8</sub>	1484.3	99.1	294.9	216.6	78.3	—
DCIAcC <sub>9</sub>	1584.1	99.8	294.3	217.4	76.9	—
DCIAcC <sub>10</sub>	1684.0	99.9	294.8	218.0	76.8	—
DCIAcC <sub>12</sub>	1884.8	200.8	295.2	217.6	77.6	—
DCIAcC <sub>14</sub>	2085.3	200.3	294.7	217.7	77.0	—
DCIAcC <sub>16</sub>	2287.0	201.7	205.9	218.7	77.2	—
TCIAcC <sub>6</sub>	1366.7	98.4	375.6	216.4	78.0	81.2
TCIAcC <sub>7</sub>	1465.1	98.7	373.4	215.3	78.2	79.9
TCIAcC <sub>8</sub>	1563.8	98.7	374.4	216.6	78.3	79.5
TCIAcC <sub>9</sub>	1663.3	99.5	373.5	217.4	76.9	79.2
TCIAcC <sub>10</sub>	1762.7	99.4	373.5	218.0	76.8	78.7
TCIAcC <sub>12</sub>	1963.0	200.3	373.4	217.6	77.6	78.2
TCIAcC <sub>14</sub>	2163.5	200.5	372.9	217.7	77.0	78.2
TCIAcC <sub>16</sub>	2364.9	201.4	373.8	218.7	77.2	77.9
MBrAcC <sub>6</sub>	1284.4	—	293.3	—	—	—
MBrAcC <sub>7</sub>	1384.2	99.8	292.5	—	—	—
MBrAcC <sub>8</sub>	1484.1	99.9	294.7	—	—	—
MBrAcC <sub>9</sub>	1584.6	100.5	294.8	—	—	—
MBrAcC <sub>10</sub>	1684.8	100.2	295.6	—	—	—
MBrAcC <sub>12</sub>	1885.3	200.5	295.7	—	—	—
MBrAcC <sub>14</sub>	2086.2	200.9	295.6	—	—	—
MBrAcC <sub>16</sub>	2287.6	201.4	296.5	—	—	—
MIAcC <sub>6</sub>	138.23	—	391.2	—	—	—
MIAcC <sub>7</sub>	1481.7	99.4	390.0	—	—	—
MIAcC <sub>8</sub>	1581.2	99.5	391.8	—	—	—
MIAcC <sub>9</sub>	1681.3	100.1	391.5	—	—	—
MIAcC <sub>10</sub>	1782.0	100.7	392.8	—	—	—

(Continued on p. 146)

TABLE II (continued)

Esters	<i>I</i>	$\Delta I_{CH_2}$	$\Delta I_{X,2X,3X}$	$\Delta I_{ICl}$	$\Delta I_{IICl}$	$\Delta I_{IIICl}$
TFAcC <sub>6</sub>	830.8	—	-160.3			
TFAcC-	927.2	96.4	-164.5			
TFAcC <sub>8</sub>	1026.3	99.1	-163.1			
TFAcC <sub>9</sub>	1123.6	97.3	-166.2			
TFAcC <sub>10</sub>	1220.0	96.4	-169.2			
TFAcC <sub>12</sub>	1418.0	198.0	-171.6			
TFAcC <sub>14</sub>	1617.4	199.4	-173.2			
TFAcC <sub>16</sub>	1816.4	199.0	-174.7			

—  $I(ClAcC_1)$ . The apparent dependence of the values of the increments of the retention indices for methylene groups ( $\Delta I_{CH_2}$ ) and chlorine atoms ( $\Delta I_X$ ) on the structure of the esters is shown in Figs. 1 and 2. Fig. 1 does not show the dependence of the retention indices of bromo- and iodoacetates on the carbon number of the alcohol moiety as their values are too close to the  $I$  values of the dichloro- and trichloroacetates. For the same reason, Fig. 2 does not show the dependence of retention indices on the carbon number for bromoacetates.

It can be seen that, in the case of the chloro-derivatives, the retention indices of

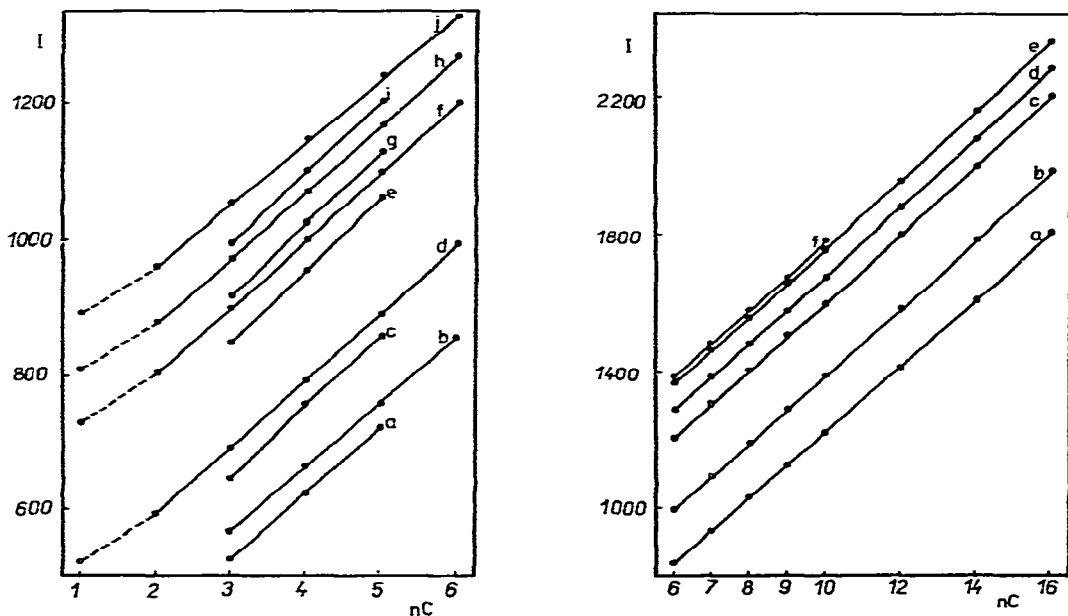


Fig. 1. Dependence of retention indices of  $C_1$ - $C_6$  alkyl esters on carbon number in the alcohol moiety, obtained from measurements using an OV-101 column at 80°C. Compounds: a =  $C_3$ - $C_5$  isoalkyl trifluoroacetates; b =  $C_3$ - $C_6$  *n*-alkyl trifluoroacetates; c =  $C_3$ - $C_5$  isoalkyl acetates; d =  $C_1$ - $C_6$  *n*-alkyl acetates; e =  $C_3$ - $C_5$  isoalkyl chloroacetates; f =  $C_1$ - $C_6$  *n*-alkyl chloroacetates; g =  $C_3$ - $C_5$  isoalkyl dichloroacetates; h =  $C_1$ - $C_6$  *n*-alkyl dichloroacetates; i =  $C_3$ - $C_5$  isoalkyl trichloroacetates; j =  $C_1$ - $C_6$  *n*-alkyl trichloroacetates.

Fig. 2. Dependence of retention indices of  $C_6$ - $C_{10}$  *n*-alkyl esters on carbon number in the alcohol moiety obtained from measurements using an OV-101 column at 200°C. Compounds: a = trifluoroacetates; b = acetates; c = chloroacetates; d = dichloroacetates; e = trichloroacetates; f = iodoacetates.

the esters increase with increasing chlorine number, as well as with the weight of the adding halogen atom, respectively. The increases in the retention indices of the lower halogenated esters are 202–211 for the first chlorine atom, 268–274 for the first bromine atom and 350–375 for the first iodine atom, while those for the higher halogenated esters are 215–219 for the first chlorine atom, 292–297 for the first bromine atom and 390–393 for the first iodine atom. The increments in the retention indices for the second and third chlorine atoms introduced into the chloro- and dichloroacetate molecules are lower than that for the first one. However, for introduction of the three fluorine atoms into the acetates the increments in the retention indices become increasingly negative. This different behaviour of fluorinated compounds can be used to make easier the analysis of hydroxy compounds by converting them into their fluorine derivatives. The separation of a mixture of lower halogenoacetates is shown in Fig. 3.

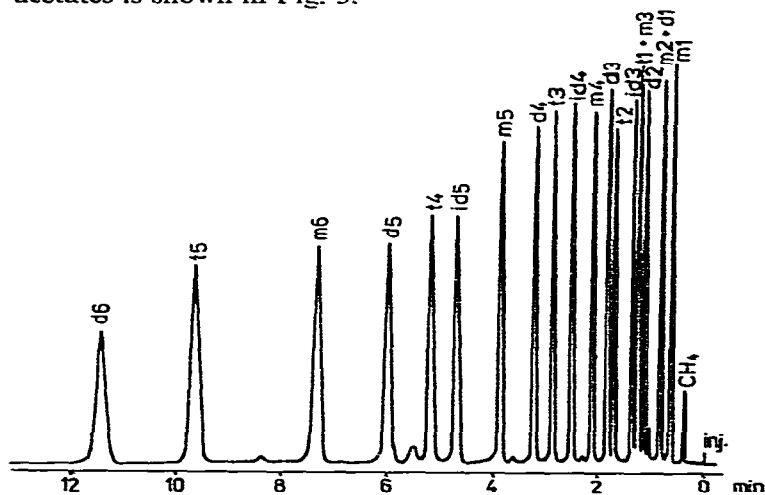


Fig. 3. Chromatograms of the separation of *n*-alkyl esters monochloroacetic (m1–m6), dichloroacetic (d1–d6) and trichloroacetic (t1–t5) acids and of isoalkyl esters of dichloroacetic acid (id3–id5) using an OV-101 column (15 m × 0.22 I.D.) at 80°C.

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